Control of Corrosion in Water Ballasted Avgas Fueling Systems by pH Adjustment

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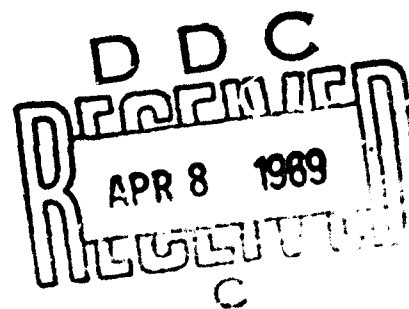
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ABSTRACT

Control of aviation gasoline corrosiveness continues to be a fleet problem. The corrosion results from corrosive sulfur compounds produced by sulfate reducing bacteria which are active in the sea water used to ballast the gasoline storage tanks. This report suggests that short term control can be effected by raising the pH of the sea water and thereby retaining any hydrogen sulfide in the ballast water. A pH of 9.5 to 10.0 is advisable and could be attained by the addition of one pound of sodium hydroxide per 1,000 gallons of water used for gasoline displacement.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

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INTRODUCTION

Aviation gasoline (Avgas) storage tanks on shipboard are designed to eliminate any vapor space. This procedure reduces the explosion hazard in a tank by limiting the volume of fuel vapor pre-mixed with air. The limitation of vapor space is accomplished by ballasting the tanks with sea water, which is also used to displace the aviation gasoline into the fueling system for operational use. Thus the Avgas tanks normally contain sea water.

The Navy has experienced problems with microbiological contamination in this method of operation. Sulfate reducing bacteria have been particularly troublesome in this system. These microorganisms utilize the sulfate in sea water (or other source) as a hydrogen acceptor and form sulfide and/or free sulfur as the product. Either one of the products turns the fuel "sour" and makes it corrosive to metals. This is detrimental to aircraft fuel systems and to shipboard storage tanks.

A review of some previous Navy difficulties with shipboard Avgas systems and suggestions for control of sulfate reducing bacteria has been presented (1). A serious incident of corrosive Avgas aboard the U.S.S. IWO JIMA (LPH-2) has been attributed to the presence of sulfate reducing bacteria in the Avgas storage tanks (2). A comprehensive report of the development and resolution of this particular difficulty has been made by the Naval Ship Engineering Center, Philadelphia Division (3). As in previous experience, it was found that the addition of sodium chromate, an effective biocide for sulfate reducing bacteria, to tank water bottoms did not eliminate the problem. The laboratory observation of sulfide oxidation to free sulfur and sulfate by chromate ion is a factor in this situation. The continuing difficulty with the U.S.S. IWO JIMA gasoline after drainage of the tanks, treatment with high pressure water streams, and incorporation of sodium chromate in the ballast water was due to the production of free sulfur by the action of chromate ion on the sulfide contained in the scale remaining in the tanks. The IWO JIMA corrosion problem was ultimately handled by sand-blasting to remove scale, covering the tank walls with Devran coating material and adding sodium chromate to the ballast water (3).

Continuing field problems have been reported recently by Collmus of the Navy POL Technical Assistance Team (4). The role of sulfate reducing bacteria in these corrosion difficulties has been confirmed by Klemme (5).

As with the U.S.S. IWO JIMA, the best suggestion for control of the Avgas corrosion problem is to sandblast and coat the storage tanks and institute the addition of sodium chromate to the ballast water. However, a short term solution which could keep ships operational until the time for normal overhaul is needed and could bring significant relief in the many corrosion incidents being reported from the field.

Hydrogen sulfide, a major corrosive product formed by sulfate reducing bacteria, is a weak acid. At a pH of 8, normal for sea water, H_2S is distributed in the water phase and in the fuel phase. Raising the pH would alter the distribution ratio between water and fuel since the salt, NaSH, would be only slightly soluble in Avgas. The amount in the acid form can be calculated for a single-phase aqueous system by using the ionization constants for H_2S (K_I) and for water (K_w) as follows:

$$[H_2S] = \frac{K_w \; [HS^-]}{K_I \; [OH^-]}$$

Since $[HS^-] = [HS^-]_{initial} - [H_2S]$,

$$[H_2S] = \frac{1.75 \times 10^{-7} [HS^-]_{initial}}{[OH^-] + 1.75 \times 10^{-7}}$$

Typical H_2S concentrations in the water phase are shown in Table 1 for different values of pH and initial NaSH concentration. These calculations indicate that most of the hydrogen sulfide could be retained in the water phase by addition of alkali and thus reduce the corrosive reaction of Avgas.

TABLE I

H_2S CONCENTRATION AT DIFFERENT pH VALUES

	H_2S Concentration (molar)		
pH	$[HS^-]_{init.}$ = 0.01 molar	$[HS^-]_{init.}$ = 0.022 molar	$[HS^-]_{init.}$ = 0.10 molar
7	64×10^{-4}	140×10^{-4}	640×10^{-4}
8	15	33	150
9	1.7	3.8	17
10	.18	.38	1.8
11	.018	.038	.18
12	.0018	.0038	.018

EXPERIMENTAL RESULTS FROM pH ADJUSTMENT

Aviation gasoline was stored for two or more days over treated water in tightly capped brown glass bottles. The samples, which comprised 200 ml of each phase, were vigorously mixed for two 15 minute periods during the storage period. The Avgas was tested for corrosiveness at the conclusion of the storage period by the Copper Strip Corrosion Test (ASTM Method D 130). The fuel sample was filtered by gravity through a paper filter to insure the absence of water during the corrosion test.

The water phase was prepared by mixing 100 ml of 0.1 N sodium hydroxide containing 0.15% $[H_2S+HS^-]$ with 100 ml of a buffered solution. Thus, the concentration in the aqueous phase was 0.075% $[H_2S+HS^-]$ (0.022 molar), which is 80% of the concentration which could be attained if all of the sulfate in sea water were converted to sulfide. This is higher than would be expected in field situations. The pH of the water phase was measured after the storage period.

The copper corrosion test results are shown in Table 2. Great improvement is evident as the water phase pH is increased. At 9.6 the tarnish is only slight and at 9.8 the Avgas has a 1 b rating, which is satisfactory for a specification fuel. In a large storage tank where a lower sulfide content would be expected and equilibrium would be reached very slowly, a pH above 9.5 should give adequate control of H_2S contamination in Avgas.

TABLE II

COPPER STRIP CORROSION

Measured pH	Cu Strip Code
7.4	4 b -- corrosion
7.6	4 a -- corrosion
8.7	2 c -- moderate tarnish
9.2	2 c -- moderate tarnish
9.6	2 a -- moderate tarnish
9.8	1 b -- slight tarnish
9.8	1 b -- slight tarnish
10.1	1 b -- slight tarnish
11.8	2 a -- moderate tarnish
Blank (not stored over H_2O phase)	1 a -- slight tarnish

A visual presentation of the trend can be seen in the attached color photograph. The improvement with pH is noteworthy. The comparison of the test strips with the standards after photography is not completely reliable and the readings presented in Table II are much preferred. These are the visual interpretations made immediately after the completion of the corrosion test.

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SELECTION OF ALKALI FOR pH CONTROL

A number of inorganic bases were considered for adjustment of sea water pH. Ammonium hydroxide must be ruled out on the basis that it would serve as a nitrogen source for bacteria. Likewise, phosphate salts such as Na_2HPO_4 and Na_3PO_4 can be eliminated since either would serve as a phosphorus source for bacteria. Calcium hydroxide may be used, but large volumes of fresh water would be required because of the low solubility of this base. Barium hydroxide is a poor selection since much excess barium ion would be required to precipitate the sulfate ion in sea water. Lithium hydroxide would be the best material from a weight basis because of its low equivalent weight. The commercial form is the hydrate, however, and as such it would offer no advantage over sodium hydroxide. Also, it is more expensive.

Sodium carbonate, sodium hydroxide and potassium hydroxide are the best choices. The first affords a pH of 9.6 by the addition of 6.25 lb. per 1,000 gal. of sea water. This material begins to precipitate calcium carbonate above 9.6 pH, however, and 31 lb. gives a pH of 9.8. Sodium hydroxide, on the other hand, gives a pH of 9.9 with 1.1 lb. per 1,000 gal. of sea water. This corresponds to three milliequivalents of alkali per liter. About 40% more KOH than NaOH would be required to attain the same pH. On the basis of the above discussion, NaOH is selected as the best material for adjustment of sea water pH. Because of the tremendous buffering capacity of sea water (105 meq. of Magnesium/liter), adjustment of the pH above 10 is impractical. At this pH, magnesium hydroxide begins to precipitate.

SUGGESTED PROCEDURE FOR pH ADJUSTMENT IN FIELD

A ship desiring to try pH adjustment as a control measure for hydrogen sulfide should first discard all contaminated Avgas and flush the storage tanks with clean sea water for 24 to 48 hours. Good quality Avgas should then be loaded. If usage rate is low, fuel should be limited to the inner tank only. After estimating the amount of sea water in the fuel tank, one lb. of technical grade NaOH should be added for each 1,000 gal. of water. This can be accomplished by adding 10 lb. of solid to 30 gal. of fresh water with stirring. After complete solution, this caustic solution can be pumped into the fuel tank and the procedure repeated until the desired amount is added. Subsequent additions must be made as Avgas is used. Caustic addition must be related to the use rate and a volume of 5,000 gal. is suggested as a convenient amount for periodic additions. The mixing drum and

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lines must be flushed with fresh water at the conclusion of each addition operation. Monitoring is extremely desirable during the initial months of the treatment described above. Measurement of the aqueous phase pH is desirable as well as tests for sulfate reducing bacteria in this phase. In addition, Avgas corrosiveness should be examined by the Copper Strip Corrosion Method. The pH measurement can conveniently be made with short range pH paper. Sampling procedures for this measurement are important. At least 2 days should be allowed after caustic addition before sampling from the storage tank. This would insure that the material added was mixed throughout the tank. Samples must be collected in clean containers after adequate flushing of the sampling lines.

Sodium hydroxide is a __strong__ caustic and __protective__ equipment must be used while handling the solid and the solution.

DISCUSSION OF pH CONTROL

The major product formed by sulfate reducing bacteria is hydrogen sulfide. The data presented in this report show that H_2S can be controlled with respect to Avgas corrosiveness by adjustment of the aqueous phase pH. Free sulfur has been reported in an Avgas system with a vapor space and H_2O layer contaminated with sulfate reducing bacteria (6). Wachs, et. al., feel that H_2S is the primary product of bacterial degradation and that free sulfur is formed by oxidation in the fuel phase. The possibility of direct formation of free sulfur by the bacteria cannot be eliminated on the basis of present knowledge, however. If free sulfur is a significant product of bacterial action, pH adjustment of the H_2O phase would not be effective in controlling corrosiveness in aviation gasoline.

Another concern with pH adjustment is the effect on fuel additives. Of particular concern are tetraethyl lead, ethylene dibromide and the fuel antioxidant. Experience with these additives indicates that little hydrolysis or extraction would be expected at a pH of 10 or less (7).

Although pH adjustment can be expected to control corrosiveness of aviation gasoline it would not eliminate sulfide corrosion of the iron storage tanks. Hence it can be suggested only as a temporary solution to the sulfate reducing bacteria contamination problem. As discussed earlier, a much better, longer-term solution is the use of sodium chromate in the water bottoms after the tanks have been thoroughly cleaned.

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OVER WATER

8.7   7.6
PHASE

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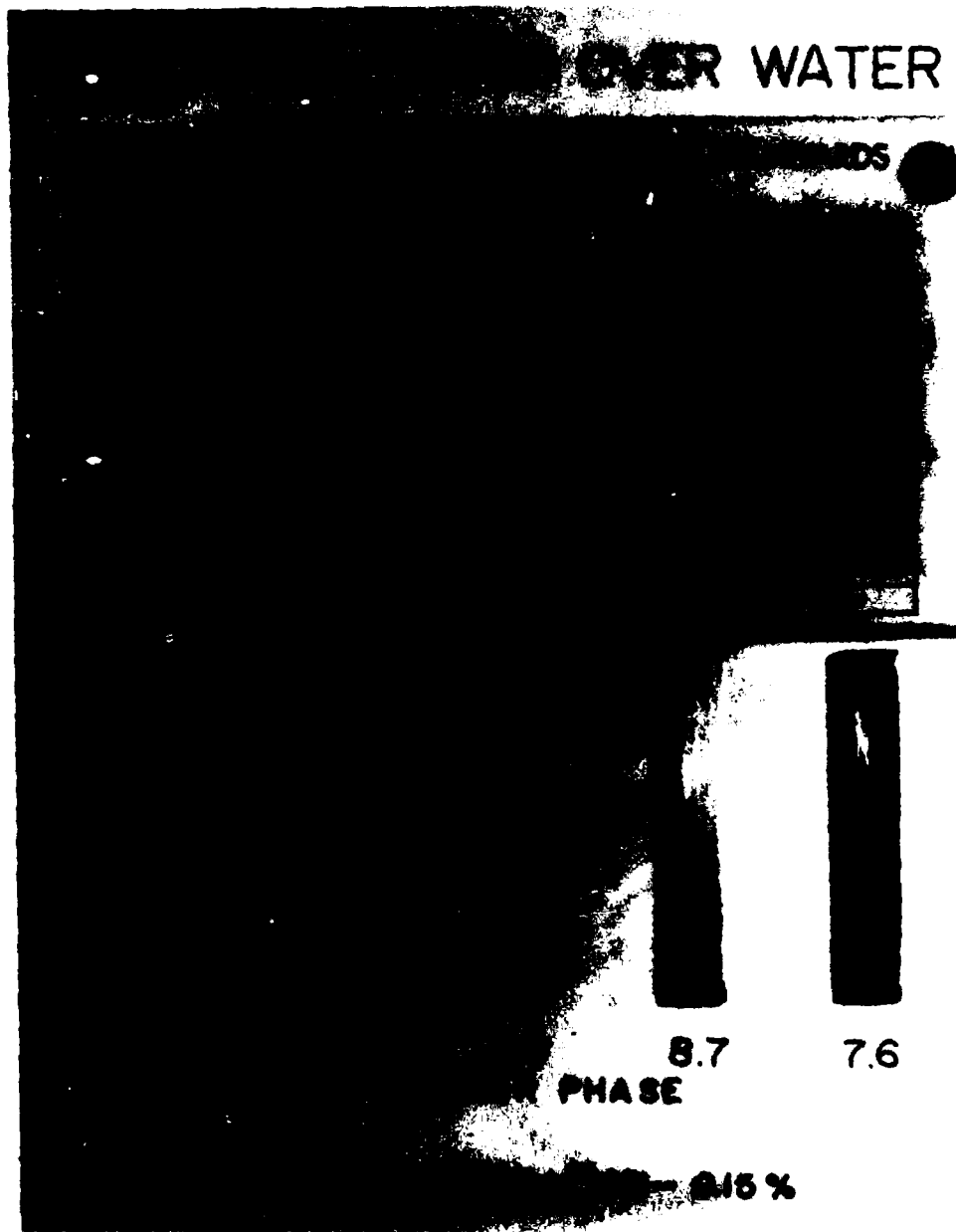
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Corrosive reaction of Avgas						
Sulfate-reducing bacteria						
Short-term control						
Adjustment of sea water pH						

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